

1.022.751

PATENT SPECIFICATION

NO DRAWINGS

1.022.751



Date of Application and filing Complete Specification: Aug. 15, 1962.

No. 31375/62.

Application made in Switzerland (No. 9593) on Aug. 16, 1961.

Complete Specification Published: March 16, 1966.

© Crown Copyright 1966.

Index at acceptance:—B6 G3B; C2 C(P1L1, P2L12B, P2L14, P2L18C, P2L19F, P2L26B, P2L26D, P2L26F, P3B13, P3B14A, P3B19E, P7); C4 P(1A1B1, 1A1C2A, 1A1C3, 1A2A1, 1A2B1, 1A2B2B, 1A3, 1A4A, 1F5, 1F6, 2G2CX, 2G5A, 2G5C6, 2H3, 2H5, 2H11, 2H15, 2H21, 2HX, 3E, 8A1A, 8A1B, 8B1, 8C3, 8D2, 8E, 9A3A4, D1M, D1N, D1S, D1T, D1X, Q4A8, Q4B12)

Int. Cl.:—B 44 d // C 07 f, C 09 b

COMPLETE SPECIFICATION

Process for Dyeing Aluminium Oxide Layers

We, DURAND & HUGUENIN A.G., a Swiss corporation, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to a process for dyeing aluminium oxide layers produced on aluminium. 5

It is known that oxide layers produced on aluminium can be dyed, for example, with inorganic pigments. Organic dyestuffs, however, are preferably used to dye aluminium oxide layers, because they are simpler to apply than inorganic pigments and they also enable numerous tints to be produced. Thus, a wide variety of organic dyestuffs have already been proposed for the dyeing of aluminium oxide layers, varying namely both with respect to their dyeing properties and their chemical constitution. Acid, water-soluble, organic dyestuffs are primarily of practical importance. 10

It has now been discovered that organic dyestuffs containing at least one acid group of an acid of pentavalent phosphorus, arsenic or antimony are particularly suitable for dyeing aluminium oxide layers. 15

By "aluminium oxide layers" there are to be understood such oxide layers as are capable of absorbing organic dyestuffs as a result of their adsorption capacity and their large internal surface. Such oxide layers can be produced both by chemical methods, e.g. by oxidation with chromates, and especially by anodic-electrolytic methods. Suitable anodic processes are, for example, the chromic acid, oxalic acid and, especially the sulphuric acid processes. 20

By "aluminium" not only pure aluminium is meant, but also alloys of aluminium with various other elements such, for example, as Cu, Mg, Mn, Si, Ni, Zn, Pb, Cd, Ti, which act in a manner similar to aluminium with respect to oxidation. Accordingly, the term "aluminium oxide layers" denotes oxide layers on aluminium and on the aforesaid aluminium alloys. 25

The dyeing of aluminium oxide layers may be effected by impregnation, for example, by painting, printing or spraying, or dying in a dye bath. The dyestuff is advantageously employed in a partially or completely dissolved form. For this purpose, both organic solvents such, for example, as ethyl alcohol, acetone or dimethylformamide, and inorganic solvents such, for example, as water, may be used, so far as the dyestuff is at least partially soluble in the respective solvents. For practical and economical reasons, dyeing in an aqueous dye bath is primarily desirable. 30

Dyestuffs containing at least one of the aforesaid acid groups excel, as tests have shown, in their particularly high affinity for aluminium oxide layers. Such dyestuffs have hitherto not been used for dyeing aluminium oxide layers. 35

It is further known that the affinity of conventional dyestuffs for aluminium oxide layers can be greatly impaired by even small amounts of foreign ions. One is therefore often forced to use softened water to prepare the dye baths and replace water lost as a result of evaporation, which is uneconomical. 40

One is forced in practice to use large dye baths, by reason of the various shapes and sizes of the aluminium oxide articles to be dyed, so that generally, when dyeing aluminium oxide articles, only a small part of the dyestuff dissolved in the dye bath is extracted. Since, however, a renewal of the bath is uneconomical, one is forced to dye in the same bath, that is to say, the dyestuff solution is not renewed after the dyeing, but brought again to the original concentration by the addition of dyestuff. This dyeing process causes an increase of foreign ions which cannot be avoided in practice, for example, ions of salts which are always present in the commercial dyestuffs, of salts resulting from the oxidation process and adhering to the aluminium articles, or of compounds used to adjust the pH value of the dye bath. Practice has shown that the presence of such salts can reduce the affinity for aluminium oxide of conventional dyestuffs so greatly that a complete renewal of the dye bath becomes necessary even if the dyestuff is still present in the original concentration.

It has now surprisingly been found that dyestuffs containing at least one acid group of an acid of phosphorus, arsenic or antimony do not exhibit this considerable, uneconomical disadvantage, but can be used dissolved either in hard water or water enriched with the usual salts. It was even noticed that the affinity of the dyestuff solutions is, in certain cases, even increased in the presence of or upon the addition of certain salts.

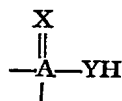
Aluminium articles having an aluminium oxide layer, which has been dyed by the process of this invention, do not bleed when kept in water and upon sealing of the oxide layer. Bleeding has hitherto often been unavoidable, even when taking all precautionary measures, so that the production of uniform dyeings has been difficult.

Furthermore, the affinity of dyestuffs containing at least one of the aforesaid acid groups for aluminium oxide is, unlike that of most of the hitherto used dyestuffs, hardly influenced by a pH value of the dyebath in the conventional range of 4—8. The often complicated adjustment and maintenance of a constant pH value of the dye bath is thus no longer necessary.

Aluminium oxide layers are usually dyed at temperatures between 55 and 65° C., since, when dyeing at room temperature, dyeings are generally obtained that are weaker or bleed more strongly in water. However, dyestuffs containing at least one of the aforesaid acid groups can also be applied without disadvantage at room temperature.

Dyestuffs containing at least one of the aforesaid acid groups, when added in small concentrations to the sealing bath, also prevent the formation of oxide layers which can be rubbed off. [Process according to F. Modic, Aluminium 35, 382 (1959) and 36, 457 (1960)].

The acid groups of pentavalent phosphorus, arsenic or antimony are preferably groups of the formula



in which A represents a phosphorus, arsenic or antimony atom, X and Y represent an oxygen or sulphur atom, and A is bound by at least one of the two free valencies to a carbon atom of a dyestuff molecule directly or through an oxygen, sulphur or nitrogen atom, and, if not so bound by the second free valency, is bound by the latter valency to a hydrogen atom or a hydroxyl, mercapto, alkyl, aryl, alkoxy or aryloxy group. The acid group is preferably bound directly to a carbon atom of a dyestuff molecule. One or more of these acid groups may be bound to the same dyestuff molecule. The acid group may be derived from one of the following compounds: phosphinic, arsenic or stibinic acid, phosphonic, arsonic or stibonic acid, thiophosphonic or thioarsonic acid, amido- or diamido- phosphoric acid, and monoesters of phosphonic acid or of phosphoric acid. The arsonic acid group, and more particularly the phosphonic acid group, are advantageous.

The chemical constitution of the dyestuffs used in the process of the invention, which contain at least one of the aforesaid acid groups is relatively unimportant as regards the affinity of the dyestuff for aluminium oxide. Widely varying classes of dyestuffs are therefore suitable such, for example, as nitro, triarylmethane, xanthene, acridine, aminoketone, quinoline, anthraquinone, phthalocyanine, monoozo, disazo, polyazo and azomethine dyestuffs. Combinations of dyestuffs of two different classes are also suitable such, for example, as azoanthraquinone and azophthalocyanine dyestuffs. Dyestuffs are further suitable which contain a group capable of forming a com-

plex with a metal, for example, an *o*-hydroxycarboxyphenyl or an *o*:*o*'-dihydroxyazo group, or those which contain a heavy metal in complex union.

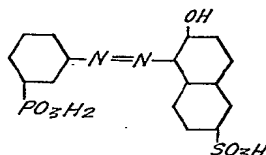
As dyeing in aqueous solution is of industrial importance, those dyestuffs are primarily of interest which contain in addition to the aforesaid acid groups, other water-solubilizing groups, in particular sulphonic acid groups, to increase the water-solubility. If desired, however, anodically oxidized aluminium may be printed with a dyestuff paste according to the film screen printing process.

Only a small number of dyestuffs that are suitable for the process of the invention are known from the literature. However, they can be prepared by methods in themselves known. They may be synthesised, for instance, by starting from intermediate products that contain at least one of the above defined acid groups. Alternatively, the acid groups may be introduced into the dyestuff molecule. A particularly suitable process for producing the dyestuffs used in accordance with the invention consists in reacting an intermediate product or dyestuff containing a reactive halogen atom with an aliphatic or aromatic amino- or hydroxy- compound containing at least one of the said acid groups. Alternatively, a compound containing a reactive halogen atom in addition to at least one of the said acid groups may be reacted with an intermediate product or dyestuff containing an amino and hydroxyl group. Azo-dyestuffs can be obtained, for instance, by reacting a diazo-component with a coupling component, at least one of which components contains at least one of the said acid groups. Such coupling components may belong, for example, to the benzene, naphthalene, acyl-acetylamine, pyrazolone or quinoline series. If the azo-dyestuff formed contains one or more groups capable of forming metal complexes, it may be converted by known methods into a complex heavy metal compound.

The following Examples illustrate the invention, the parts and percentages being by weight, unless otherwise stated, and the temperatures being degrees Centigrade.

EXAMPLE 1

A degreased piece of aluminium is anodically oxidized in 20% sulphuric acid at a current density of 1.5 amp/dm² for 30 minutes at 18—20° to form an oxide layer having a thickness of 10 microns, is rinsed in running water for 15 minutes and then dyed in a dyebath which was produced by dissolving 1 part of the dyestuff of the formula



in 1000 parts of non-softened water, at a pH of 7.0 and at room temperature for 30 minutes. A vivid golden yellow dyeing is obtained which does not bleed upon sealing in boiling water.

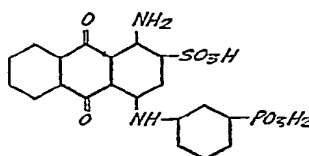
If a dyestuff of the above formula is employed which has a SO₃H group instead of the PO₃H₂ group, and the dyeing is performed under the same conditions, the piece of aluminium is completely decoloured in the sealing bath as a result of bleeding.

The dyestuff used in this Example may be prepared as follows: 17.3 parts of 3-aminophenyl-phosphonic acid are dissolved in 200 parts of water with sodium hydroxide solution to form a neutral solution. 25 parts by volume of hydrochloric acid (33%) are added and the solution is diazotized after having been cooled to 5—10° by the dropwise addition of an aqueous solution of 7.0 parts of sodium nitrite. The diazo solution is allowed to flow at 3—8° into a solution of 22.4 parts of 2-naphthol-6-sulphonic acid and 30 parts of sodium carbonate in 350 parts of water. Upon completion, the solution is heated until the dyestuff dissolves, 100 parts of sodium chloride are added, and the precipitated dyestuff is filtered off after having cooled.

If the 3-aminophenyl-phosphonic acid is replaced by equivalent amounts of 3-aminophenylmethylphosphonic acid or 4-aminodiphenyl arsinic acid dyestuffs with similar properties are obtained.

EXAMPLE 2

A piece of aluminium anodically oxidized according to Example 1 is dyed at 60° and at a pH of 7.0 in a bath containing 1 part of the dyestuff of the formula



5 dissolved in 1000 parts of non-softened water.

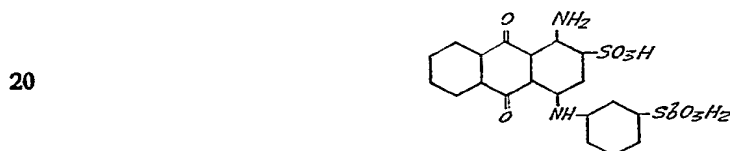
A deep blue dyeing is obtained.

Even with the addition of up to 15% sodium sulphate to the dye bath before dyeing, an equally strong dyeing is obtained.

10 If a dyestuff of the above formula is used which has a SO₃H group instead of the PO₃H₂ group, the piece of aluminium is dyed considerably fainter. In the presence of sodium sulphate, absolutely no colouring takes place.

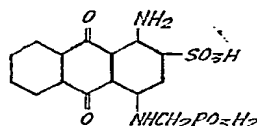
The dyestuff used in this Example may be prepared as follows: 30 parts of 1-amino-4-bromo-anthraquinone-2-sulphonic acid, 26 parts of 3-aminophenyl-phosphonic acid, 47 parts of sodium carbonate and 3 parts of copper-(I)-chloride are heated in 800 parts of water for 20 hours at 60—70°. By the addition of hydrochloric acid until an acid reaction to congo red is obtained, the dyestuff is precipitated and obtained pure by dissolving the sodium salt in water and then precipitating the same.

Dyestuffs of the following composition



Shade: blue

and

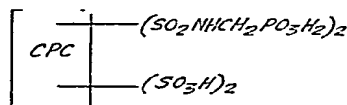


Shade: violet

25 which may be prepared in the same manner, have similar properties.

EXAMPLE 3

A piece of aluminium anodically oxidized according to Example 1 is dyed for 30 minutes at 60° and a pH of 7.0 in a bath containing 2 parts of the dyestuff of the formula



wherein CPC means a copper phthalocyanine molecule substituted in the 3:3¹:3¹¹:3¹¹¹-positions, 100 parts of sodium chloride and 1 part of nitrilo-triacetic acid in 1000 parts of non-softened water. A vivid, turquoise-blue dyeing is obtained. If the piece of aluminium is placed in non-softened water without sealing, no bleeding can be noted even after three days.

If the dyeing is performed under the same conditions but in a bath containing 2 parts of copper phthalocyanine-3:3':3'':3'''-tetra-sulphonic acid, aluminium is not coloured. On the other hand, if the dyeing is effected under conditions suitable for dyestuffs exempt of phosphonic acid groups (i.e. at a pH of 5 and in the presence of softened water), a turquoise-blue dyeing is also obtained. After being placed in non-softened water, the piece of aluminium dyed in this manner is after one day partially and after three days completely decoloured.

The dyestuff used in this Example can be prepared as follows: 29 parts of copper phthalocyanine are introduced into 220 parts of chlorosulphonic acid at 35° and stirred for 1 hour at 35° and for 4 hours at 135°. After having cooled to room temperature, one pours onto ice, the precipitated copper phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride is filtered off, slurried in ice water and neutralized with sodium carbonate. An aqueous solution of 11.5 parts of aminomethane phosphonic acid and 35 parts of sodium carbonate are added and the mixture is stirred until the reaction is completed. The dyestuff is precipitated by the addition of hydrochloric acid and is recrystallized from water.

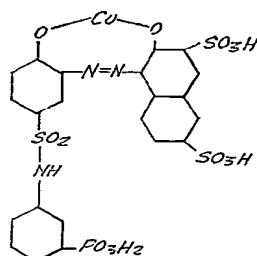
If 5.8 parts or 17.3 parts of aminomethane phosphonic acid are used instead of 11.5 parts of aminomethane phosphonic acid, dyestuffs are obtained which are also suitable for the process claimed.

If, instead of the aminomethane phosphonic acid, equivalent amounts of 3-amino-4-methylphenyl-phosphonic acid, 3-amino-4-chlorophenyl-arsonic acid or 4-amino-phenyl-stibonic acid are used, dyestuffs are obtained with similar properties.

Instead of copper phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride, copper phthalocyanine-3:4':4'':4'''-tetrasulphonic chloride, nickel phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride and chromium phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride may be used, the latter compound yielding greener shades.

EXAMPLE 4

A piece of aluminium anodically oxidized according to Example 1 is dyed at 60° in a dyebath containing 5 parts of the dyestuff of the formula



in 1000 parts of water. A red dyeing is obtained which, compared with the comparable dyestuff free from phosphonic acid groups, excels by its deeper shade and lesser bleeding upon sealling in boiling water.

The dyestuff used in this Example may be prepared as follows:

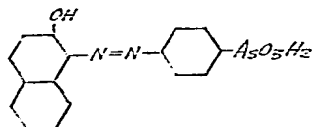
26 parts of 3-nitro-4-chlorobenzene-1-sulphonic chloride are introduced in portions at 20—30° into a solution of 17 parts of 3-aminophenyl-phosphonic acid in 100 parts of water, the pH value being maintained at 7.5 to 8.5 with diluted sodium hydroxide solution. After the reaction is completed, the condensation product is separated off by the addition of sodium chloride and filtered. The intermediate compound is heated under reflux in 100 parts of water and 30 parts by volume of caustic soda lye (30%) for 3 hours, rendered acid to congo red with hydrochloric acid and filtered off. The resulting product is introduced in portions into a boiling suspension of 30 parts of iron powder in 150 parts of water and reduced. 2 parts of sodium sulphite are now added, the suspension is rendered markedly alkaline to phenolphthalein with caustic soda solution, the iron residue is filtered off, and the filtrate neutralized with hydrochloric acid. A solution of 3-(4'-hydroxy-3'-amino-phenylsulphonylamino)-phenyl-phosphonic acid is thus obtained. A solution containing 34.4 parts of the above compound is diazotized at 5—10° by the addition of hydrochloric acid and 7 parts of sodium nitrite and introduced at 15° into a solution of 31 parts of 2-naphthol-3:6-disulphonic acid and 40 parts of sodium carbonate in 200 parts of water. After the coupling is completed, the solution is neutralized with 80% acetic acid, 25 parts of crystallized copper sulphate are added, the whole is

refluxed for 1 hour and the copper compound of the monoazo dyestuff is separated off by filtration after the addition of sodium chloride.

Equivalent amounts of 3-aminophenyl-arsonic acid or aminomethyl-phosphonic acid may be used with the same success instead of the 3-aminophenyl-phosphonic acid.

EXAMPLE 5

1 part of dyestuff of the formula



is dissolved in 20 parts of dimethylformamide and stirred into 80 parts of thickener (consisting of 8 parts of ethyl cellulose and 92 parts of xylene).

The paste is printed on anodically oxidized aluminium by the film screen printing process and dried in the air. The print is completed by sealing in boiling water and washing with benzene. An orange coloured print is obtained.

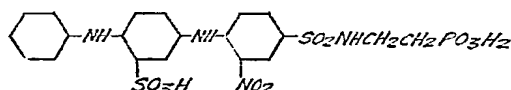
The dyestuff used in this Example is obtained by coupling diazotized 4-aminophenyl-arsonic acid and 2-naphthol.

If 4-aminophenyl-phosphonic acid or 4-aminophenyl-stibonic acid is used instead of 4-aminophenyl-arsonic acid, dyestuffs with similar properties are obtained.

The dyestuffs used in this Example may also be dyed cold on aluminium from a 1% solution in dimethylformamide.

EXAMPLE 6

A piece of aluminium anodically oxidized according to Example 1 is dyed for 30 minutes at 60° in a bath containing 2 parts of the dyestuff of the formula



in 1000 parts of water. A yellowish brown dyeing is obtained which excels in its water-fastness.

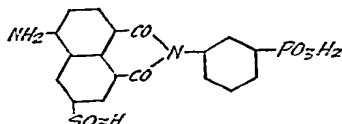
The dyestuff used in this Example can be prepared as follows: 25.6 parts of 3-nitro-4-chlorobenzene-1-sulphonyl chloride are introduced at 30—40° in portions into a solution of 12.5 parts of 2-aminoethyl-phosphonic acid in 100 parts of water. A pH value of 7—8 is maintained during the said introduction by the dropwise addition of 2N sodium carbonate solution. After the reaction is completed, the solution is rendered markedly acid to congo red with hydrochloric acid, the precipitated product is filtered off and recrystallized from alcohol.

34.5 parts of the resulting 2-(3'-nitro-4'-chlorobenzene-sulphonylamino)-ethyl-phosphonic acid and 26.5 parts of 4-aminodiphenylamine-2-sulphonic acid are dissolved in the cold in 250 parts of water with caustic soda lye to form a neutral solution. 30 g of sodium bicarbonate are then added and the whole is refluxed until the reaction is completed. The nitro dyestuff is separated off in conventional manner and freed of by-products.

Instead of 2-(3'-nitro-4'-chlorobenzenesulphonylamino)-ethyl-phosphonic acid, equivalent amounts of 3-(3'-nitro-4'-chlorobenzene-sulphonylamino)-phenyl-phosphonic acid, -arsonic acid or -stibonic acid may be used with the same success.

EXAMPLE 7

A sheet of aluminium is oxidized at 95° for 10 minutes in a solution consisting of 50 parts of sodium carbonate (anhydrous), 15 parts of sodium chromate and 1000 parts of water, rinsed for 10 minutes in running water and then dyed for 5 minutes at 60° in a dyebath consisting of 5 parts of dyestuff of the formula

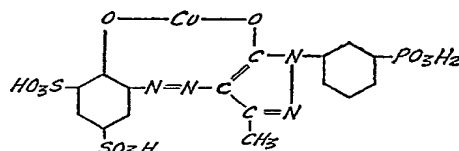


dissolved in 1000 parts of water. A matt, yellowish olive-green dyeing is obtained which excels in its water-fastness.

The dyestuff used in this Example may be prepared as follows: 15.5 parts of 4-aminonaphthalic acid-6-sulphonic acid, 8.6 parts of 3-aminophenyl-phosphonic acid and 30 parts of sodium bisulphite (anhydrous) are refluxed for 12 hours in 200 parts of water. The dyestuff is isolated as usual.

EXAMPLE 8

A degreased piece of aluminium is anodically oxidized in an oxalic acid solution consisting of 30 parts of oxalic acid, 20 parts of potassium oxalate and 1000 parts of water at a current density of 1.5 amps/dm² and a temperature of 55—60° for 30 minutes to form an oxide layer having a thickness of approximately 12 microns, rinsed for 10 minutes in running water and then dyed at 60° in a dyebath prepared by dissolving 1 part of dyestuff of the formula



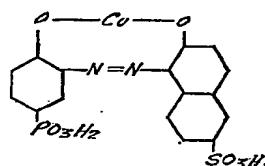
in 1000 parts of water. A golden yellow dyeing is obtained which excels in its water-fastness when kept under water and sealed in boiling water.

The dyestuff used in this example may be prepared as follows: 17.3 parts of 3-aminophenyl-phosphonic acid and 7 parts of sodium nitrite are dissolved neutral in 100 parts of water by the addition of sodium carbonate. This solution is added dropwise to a mixture of 80 parts of ice and 12.5 parts of concentrated sulphuric acid, and diazotized at 0—5°. The resulting diazo solution is added at 10° to 80 parts by volume of sodium bisulphite solution (40%) containing 19 parts of sodium carbonate and 30 parts of ice. The reaction mixture is allowed to warm to room temperature while stirring and the temperature is increased to 50° after 2 hours. After the dropwise addition of 61 parts by volume of concentrated sulphuric acid, the mixture is brought to the boiling point and this temperature is maintained for 4 hours. The cooled solution of phenylhydrazine-3-phosphonic acid is rendered slightly alkaline by the dropwise addition of concentrated caustic soda lye, 13.8 parts of acetoacetic acid ethyl ester are added at 60°, the pH is adjusted to 12 with concentrated caustic soda lye after 1 hour and the solution is heated to 95—100° for 2 hours. After cooling, the solution is rendered acid to congo red by the addition of 300 parts by volume of 2N sulphuric acid. The precipitated residue is filtered off, washed with water and dried. 16 parts of 1-phenyl-3-methyl-5-pyrazolone-3'-phosphonic acid are obtained.

The diazo compound prepared from 27 parts of 2-aminophenol-4:6-disulphonic acid is coupled at room temperature in the presence of sodium acetate with 25.5 parts of 1-phenyl-3-methyl-5-pyrazolone-3'-phosphonic acid, obtained as intermediate product, and the resulting dyestuff is converted into the complex metal compound of the above formula by heating with 25 parts of crystallized copper sulphate.

EXAMPLE 9

A sheet of aluminium is anodically oxidized for 60 minutes in a solution consisting of 5 parts of chromic acid, 0.5 parts of oxalic acid and 0.3 parts of boric acid at 40° and with a current density of 1 amp/dm² and a voltage of 25—40 volts, rinsed for 10 minutes in running water and then dyed at 60° in a dyebath produced by dissolving 1 part of dyestuff of the formula



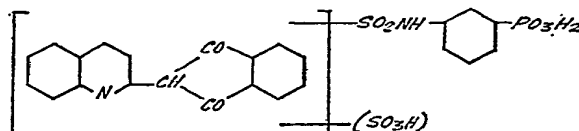
in 1000 parts of water. A matt red dyeing is obtained which, compared to the dyeing produced by the comparable dyestuff exempt of phosphonic acid groups, excels in its markedly improved water-fastness and its deeper shade.

The dyestuff used in this Example may be prepared as follows: 20.4 parts of the monoazo dyestuff prepared according to Example 1 from diazotized 3-aminophenyl-

phosphonic acid and 2-naphthol-6-sulphonic acid are dissolved in 400 parts of water at 60°. 13.8 parts of crystallized copper sulphate and 15 parts of crystallized sodium acetate are then added. 14.1 parts of hydrogen peroxide (30% strength) dissolved in 50 parts of water are added dropwise within 30 minutes, the temperature is maintained at 60° for 2 hours, the solution is then heated to 90° and the dyestuff salted out after the addition of 1.3 parts of nitrilo-triacetic acid.

EXAMPLE 10

A sheet of aluminium anodically oxidized according to Example 1 is dyed for 30 minutes at 60° and with a pH of 5.5 in a bath containing 10 parts of the dyestuff of the formula



dissolved in 1000 parts of water. A greenish yellow dyeing is obtained which excels in its non-bleeding when kept under water and upon sealing.

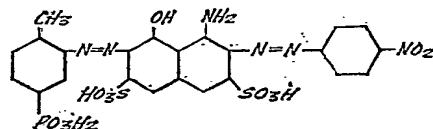
The dyestuff used in this Example can be prepared as follows: 27.3 parts of quinophthalone are introduced at 25° into 500 parts of chlorosulphonic acid and stirred for 1 hour at 25° and for 4 hours at 130°. After having cooled, the mixture is poured into ice and the precipitated sulphonic chloride is filtered off. The moist sulphonic chloride is then immediately slurried in 200 parts of water at 0°, neutralized with sodium bicarbonate and an ice cold solution consisting of 17.3 parts of 3-aminophenyl-phosphonic acid, 40 parts of sodium bicarbonate and 200 parts of water is added. After the reaction is completed, the dyestuff is separated off by the addition of sodium chloride and recrystallized from water.

Equivalent amounts of 4-methyl-3-aminophenyltrithicarsonic acid can be used instead of 3-aminophenyl-phosphonic acid.

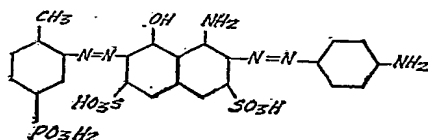
In the following Table further Examples of dyestuffs are listed which excel in a high affinity to aluminium oxide layers. The shades produced by these dyestuffs on anodically oxidized aluminium articles are given in the following Table.

TABLE

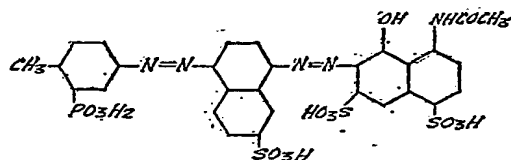
| Example | Constitution of the dyestuff | Shade produced |
|---------|------------------------------|----------------|
| 11 | | bluish black |
| 12 | | greenish black |
| 13 | | reddish blue |



bluish
black



greenish
black

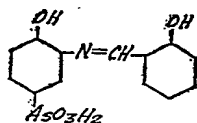


reddish
blue

TABLE—(Continued)

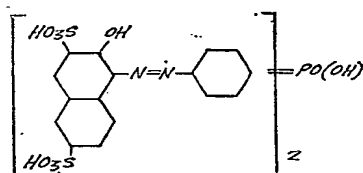
| Example | Constitution of the dyestuff | Shade produced |
|---------|------------------------------|----------------|
|---------|------------------------------|----------------|

14



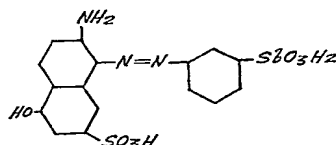
yellow

15

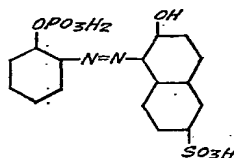


orange

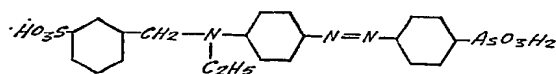
16

brownish
orange

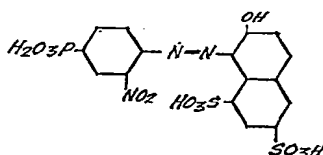
17

reddish
violet

18

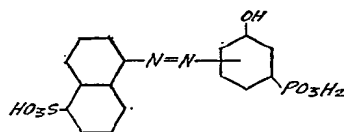
golden
yellow

19

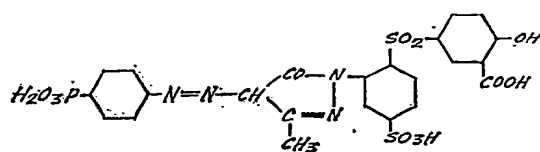


orange

20

brownish
yellow

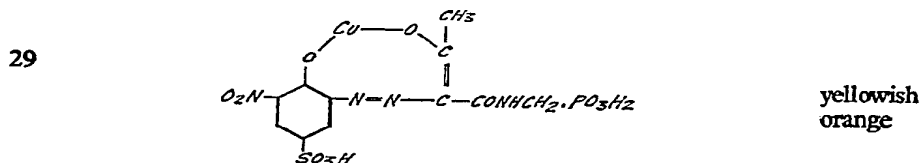
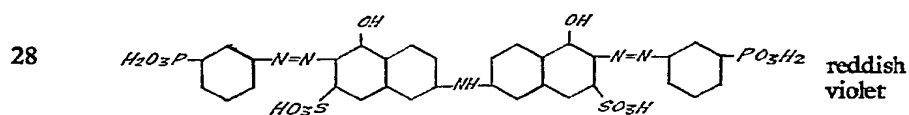
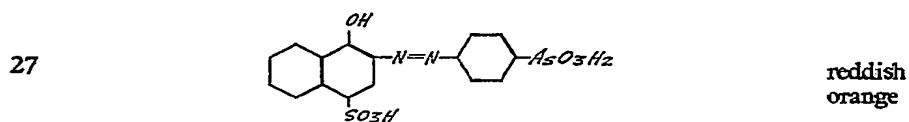
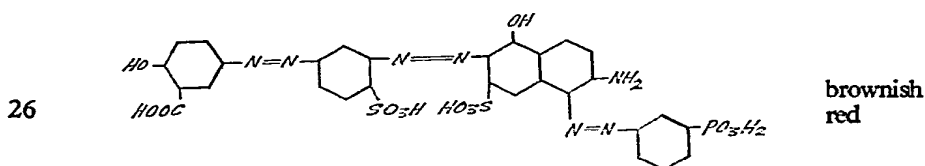
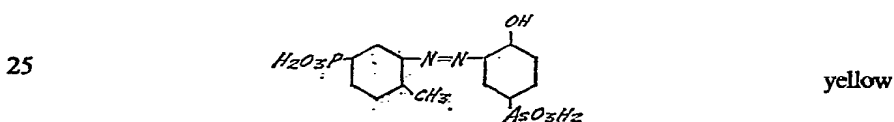
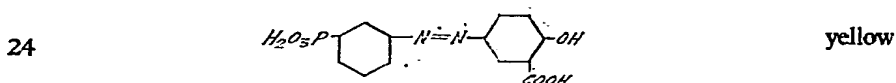
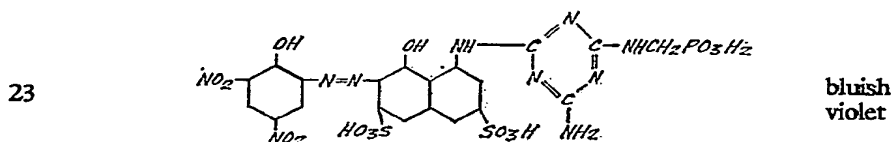
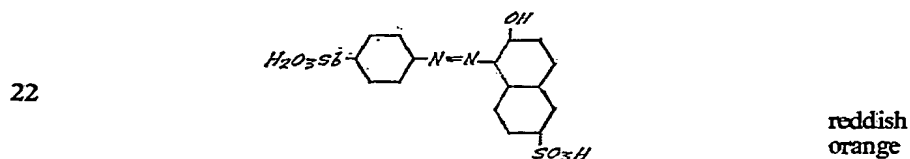
21



yellow

TABLE—(Continued)
Constitution of the dyestuff

Example Shade produced

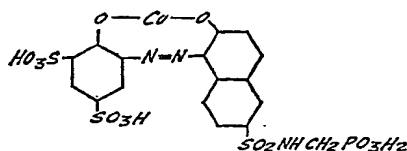


Produced from the reaction product of diketene and amino-methane phosphonic acid by coupling with diazotized 6-nitro-2-aminophenol-4-sulphonic acid and subsequent complexing with copper.

TABLE—(Continued)

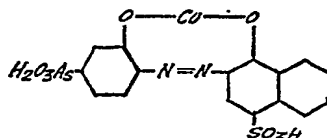
| Example | Constitution of the dyestuff | Shade produced |
|---------|------------------------------|----------------|
|---------|------------------------------|----------------|

30

bluish
red

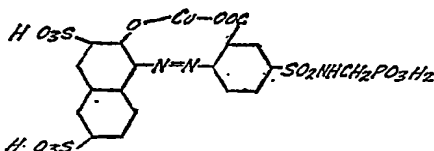
Produced by reacting 2-hydroxy-1-carboxynaphthalene-6-sulphonic chloride and aminomethane phosphonic acid, splitting off the carboxy group, coupling with diazotized 2-aminophenol-4:6-disulphonic acid and subsequent complexing with copper.

31

reddish
violet

Produced from dyestuff according to Example 27 by oxidative complexing with copper.

32



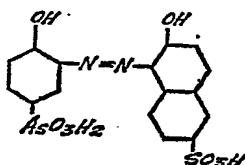
red

Produced by condensing 4-chloro-3-carboxybenzene sulphonic chloride and amino-methane phosphonic acid, reacting the labile chlorine atom with aqueous ammonia in the presence of copper powder in an autoclave at 135°, diazotizing the resulting amine and coupling with 2-hydroxy-naphthalene-3:6-disulphonic acid and converting into the complex copper compound.

33a

Copper complex of the dyestuff of the following formula

red



33b

Chromium complex of the dyestuff according to Example 33a.

violet

33c

Cobalt complex of the dyestuff according to Example 33a.

reddish
violet

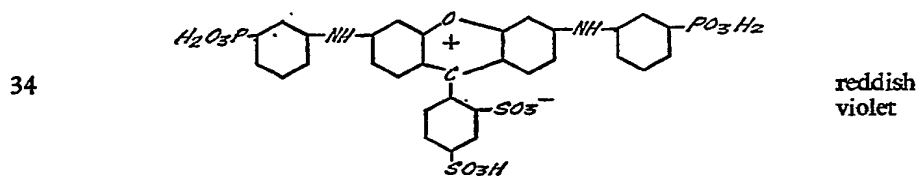
33d

Nickel complex of the dyestuff according to Example 33a.

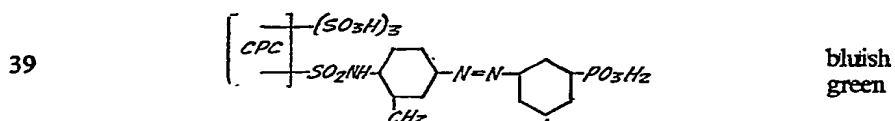
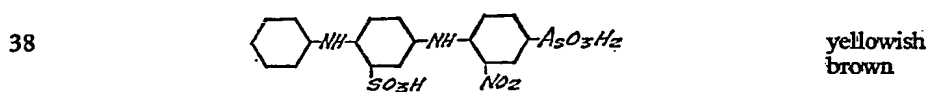
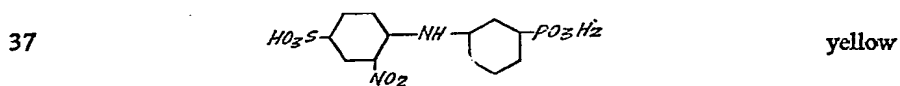
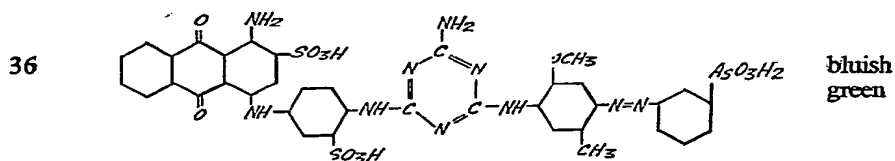
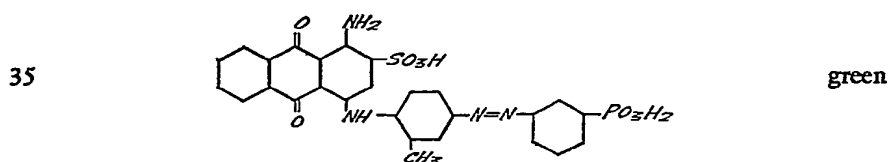
red

TABLE—(Continued)

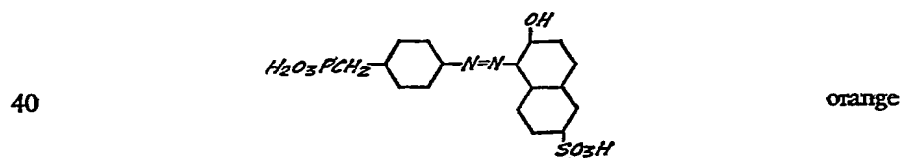
| Example | Constitution of the dyestuff | Shade produced |
|---------|------------------------------|----------------|
|---------|------------------------------|----------------|



Produced according to the process of German Letters Patent 870,270 and 895,041 (See also British Specification No. 744,972).



wherein CPC means a copper phthalocyanine molecule substituted in 3:4:11:11-position.



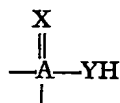
TABLE—(Continued)

| Example | Constitution of the dyestuff | Shade produced |
|---------|------------------------------|----------------|
| 41 | | golden yellow |

WHAT WE CLAIM IS:—

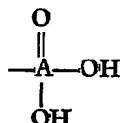
1. A process for dyeing aluminium having an oxide layer capable of absorbing organic dyestuffs or an aluminium alloy having such an oxide layer, wherein the oxide layer is dyed with an organic dyestuff containing at least one acid group of an acid of a pentavalent phosphorus, arsenic or antimony.

2. A process as claimed in claim 1, wherein the dyestuff used contains at least one acid group of the formula



in which A represents a phosphorus, arsenic or antimony atom, X and Y represent an oxygen or sulphur atom, and A is bound by at least one of the two free valencies to a carbon atom of a dyestuff molecule directly or through an oxygen, sulphur or nitrogen atom, and, if not so bound by the second free valency, is bound by the latter valency to a hydrogen atom or a hydroxyl, mercapto, alkyl, aryl, alkoxy or aryloxy group.

3. A process as claimed in claim 2, wherein the dyestuff used contains at least one acid group of the general formula



in which A represents a phosphorus or arsenic atom.

4. A process as claimed in any one of claims 1 to 3, wherein the dyestuff used contains, in addition to the said acid group or groups, at least one other group imparting solubility in water.

5. A process as claimed in any one of claims 1 to 3, wherein the dyestuff used contains, in addition to the said acid group or groups, at least one sulphonic acid group.

6. A process as claimed in claim 1, wherein the dyestuff used is any one of the dyestuffs of the formulae given in Examples 1 to 41.

7. A dyeing process as claimed in claim 1 and conducted substantially as described in any one of Examples 1 to 10.

8. Aluminium or an aluminium alloy which has been dyed by the process claimed in any one of claims 1 to 7.

ABEL & IMRAY,

Chartered Patent Agents,

Quality House, Quality Court, Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

